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APR 77 G W STUPIAN, A B CHASE

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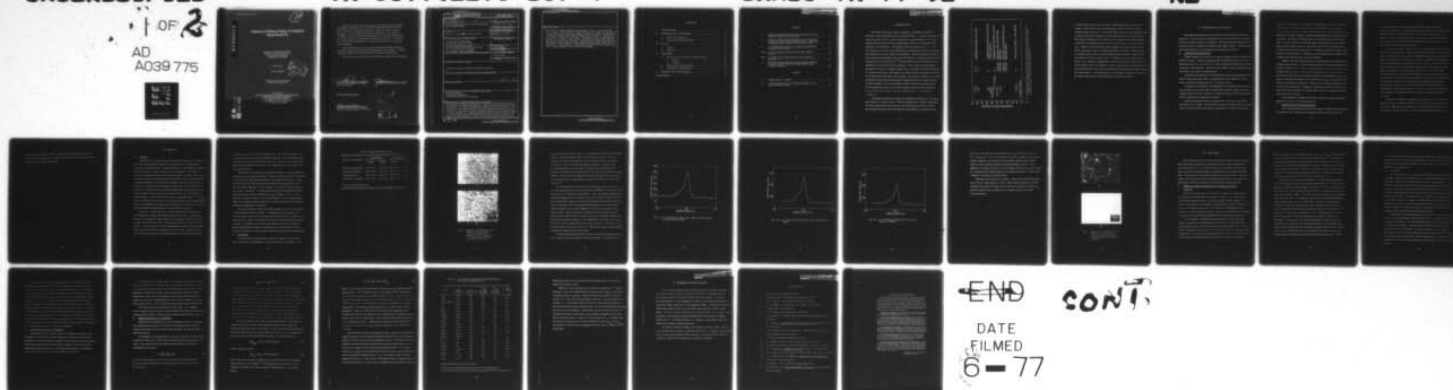
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Adhesion of Films of MoS_2 to Oxidized Metal Surfaces

Chemistry and Physics Laboratory
The Ivan A. Getting Laboratories
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El Segundo, Calif. 90245

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Interim Report





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accessible to sulfur in order for these bonds to form. On some metals, e.g., copper, it was found that surface oxygen is not present as an oxide but exists in a precursor state less tightly bound than an oxide. The formation of substrate metal-sulfur bonds by displacement of oxygen is facilitated by the existence of this precursor state. On metals with more stable surface oxides, e.g., titanium, oxygen lattice vacancies are present that again expose surface metal atoms to sulfur. Experiments in which MoS_2 films were burnished onto both oxidized metals and metal oxide single crystals are reported here. All results are consistently interpreted in terms of the nature of the oxygen initially present on the metal surface.

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I. INTRODUCTION

Transition metal layer lattice compounds, molybdenum disulfide in particular, have found application as solid lubricants.¹ A layered solid must meet two requirements in order to function as a solid lubricant: (1) it must exhibit sufficiently facile intracrystallite slip, and (2) it must adhere to the substrate to be lubricated. The question of intracrystallite slip, i.e., the low resistance of certain layered structures to shearing stresses, has already been addressed at some length in the literature. Qualitative theories attempting to relate intracrystallite slip to atomic bonding in transition metal layered compounds have been advanced,^{2,3} but the adhesion of solid lubricants to the substrate has received much less attention. In a recently published paper,⁴ the degree of surface coverage of MoS_2 films, burnished onto metal substrates by a standard technique, was shown to correlate with the atomization energies of the appropriate transition metal sulfides. Atomization energies are readily obtained from tabulated thermodynamic properties and are a rough measure of bond strengths. The most pertinent results of these prior experiments, the coverages observed on the several substrates and the substrate metal-sulfide atomization energies, are summarized in Fig. 1. A correlation is apparent.

The observed adhesion of MoS_2 was explained by Stupian et al.⁴ without any reference to surface oxides. Since all metals have a surface oxygen film at normal temperature and pressure, this omission was of some concern. Our preliminary laboratory observations of the behavior of burnished films

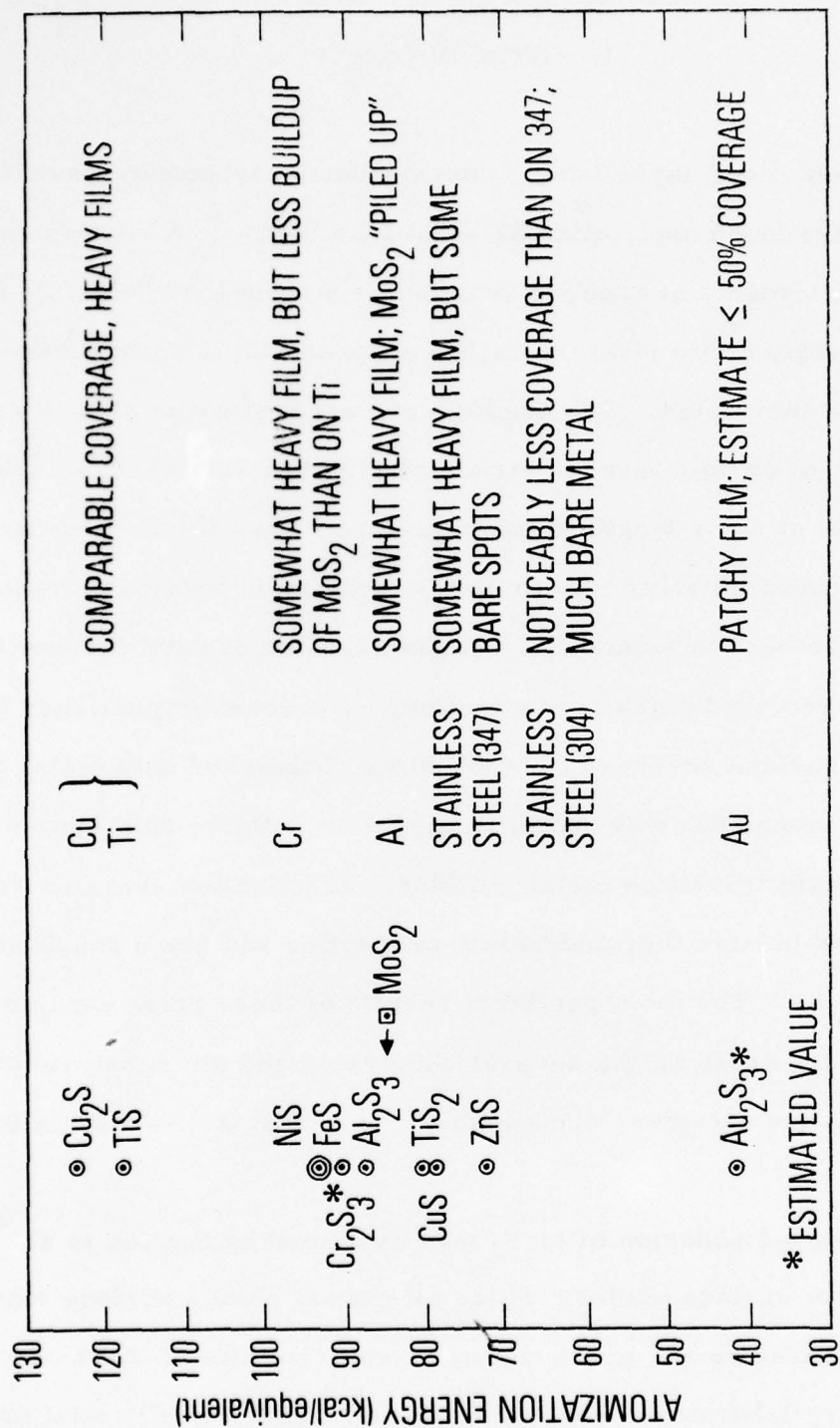


Fig. 1. Substrate Metal-Sulfur Bond Energies and the Observed Degree of Adhesion of MoS_2 Films. Substrate materials are listed in order of decreasing coverage by MoS_2 . Data taken from Stupian et al.⁴

on deliberately oxidized metal surfaces yielded apparently contradictory results. The present study was undertaken to further clarify our understanding of MoS₂ adhesion. It was found that the substrate metal-sulfur bond is indeed of primary importance in MoS₂ film adhesion, in agreement with the findings of Stupian et al.⁴ However, the substrate metal atoms must be accessible to the sulfur in order for these bonds to form. On some metals, e.g., copper, it was found that surface oxygen is not present as an oxide but in a precursor state less tightly bound than in an oxide. The formation of substrate metal-sulfur bonds by displacement of oxygen is facilitated by the existence of this precursor state. On metals with more stable surface oxides, e.g., titanium, oxygen lattice vacancies are present that again effectively expose surface metal atoms to sulfur. Experiments in which MoS₂ films were burnished onto both oxidized metals and onto metal oxide single crystals are reported here. All observations are consistently interpreted in terms of the nature of the oxygen initially present on the metal surfaces.

II. EXPERIMENTAL PROCEDURE

Burnishing experiments were carried out on both titanium and copper specimens. These metals were subjected to several preparative treatments as well as different degrees of oxidation. The burnishing experiments were also performed on oxidized and reduced TiO_2 single crystals. All specimens were characterized by x-ray photoelectron spectroscopy (XPS).

A. SPECIMEN PREPARATION

Copper samples were cut from a sheet of oxygen-free high-conductivity (OFHC) material. Titanium specimens were commercially pure ($>99.7\%$). Specimens were cut to a size ($\approx 2.2 \times 1$ cm) convenient for both burnishing and mounting for XPS analysis. Specimens were cleaned, either mechanically or chemically, and rinsed in distilled water.

Mechanical polishing was accomplished by using a polishing wheel with 600 grit paper (generally with a continuous water flow) followed, in some cases, by further polishing with a $0.3\text{-}\mu\text{m}$ Al_2O_3 slurry.

A solution of 55% H_3PO_4 , 25% CH_3COOH , and 20% HNO_3 (by volume of the concentrated acids) was used to chemically clean the copper specimens. Titanium specimens were cleaned in concentrated H_2SO_4 since the expected surface oxide (TiO_2) is soluble in this acid.

Copper was oxidized either by exposure to a heat gun or by placing specimens on a hot plate. Several distinct stages in the formation of an oxide film are clearly visible when copper is heated in air. After a few minutes

exposure to a heat gun or on a hot plate, a cleaned piece of copper develops a brownish film. The film spreads from several nucleation points until the surface appears uniform. Further heating results in a noticeably thicker gray film that, once again, appears uniform after spreading from several nucleation sites. Still further heating results in the flaking-off of a black oxide layer. Future reference to oxidized copper will include either the uniform film produced by the heat gun or the thicker uniform film obtained with the hot plate before flaking of the surface. The utility and validity of this classification is discussed later. Titanium metal was oxidized on a hot plate until a uniform gold (interference) color was obtained.

Single crystal TiO_2 specimens were nominally pure rutile grown by the National Lead Company. Spectrochemical analysis showed the impurity level in these crystals to be $\leq 0.005\%$. Experiments were carried out on the c-faces of these single crystals, which were first polished with 1- μm Al_2O_3 slurry. The crystals were then either heated at 600°C in one atmosphere of O_2 overnight or reduced by heating for 1 hr at 600°C in 1 atm H_2 . The crystals were initially colorless and transparent. Heating in an oxidizing atmosphere did not alter their appearance. Heating in a reducing atmosphere under the conditions described resulted in a nearly opaque crystal that appeared lustrous and greyish-blue to black.

The molybdenum disulfide used in this study was a commercial grade material (Molykote Z, Dow Corning Corp.).

B. APPARATUS AND MEASUREMENTS

The x-ray photoelectron spectrometer used for surface characterization of specimens was a McPherson Instrument Corporation Model ESCA 36.

X-ray excited Auger electron spectra (AES) can be obtained with the ESCA 36 spectrometer. Auger spectra are often quite useful in distinguishing different oxides, especially when used in conjunction with photoelectron spectra.^{5,6} It was convenient to use an Auger spectrometer with electron excitation (Physical Electronics Industries Model 10-500) for surface characterization of some titanium specimens.

In the present study, oxygen 1s (O 1s) x-ray photoelectron spectra were obtained for all specimens. Copper 2p photoelectron spectra, x-ray excited copper LMM Auger spectra, and Ti 2p photoelectron spectra (and sometimes electron-excited Ti LMM AES) were recorded. An XPS peak is denoted by the corresponding atomic energy level, e.g., 1s, 2p_{1/2}, whereas an Auger peak is denoted by specifying the three energy levels involved in the Auger transition using the x-ray notation for these levels, e.g., KLL, LMM. XPS survey scans covering 0-1000 eV binding energy, which should reveal all elements present on the specimen surface, were made for each specimen to ensure that results were not influenced by unexpected contaminants. Photoelectron energies were measured relative to the hydrocarbon contamination C 1s peak, assumed to be at 284.6 eV. Specimen charging was not a problem. Consistent results were obtained with the hydrocarbon reference.

Molybdenum disulfide was applied to all specimens in a reproducible manner by using a rotating steel ball covered with a lint-free cloth loaded with MoS₂. The ball was run against the specimens (in air) for 30 sec at 750 rpm at a total load of 100 g. The burnishing apparatus was the same

device used in our earlier work.⁴ Assessment of the degree of specimen surface coverage obtained was made by observation of the circular burnish spots through an optical microscope.

III. RESULTS

A. COPPER

Photoelectron and Auger electron spectra were obtained for chemically and mechanically polished copper and for copper specimens deliberately oxidized as described earlier. Both 2p photoelectron and LMM Auger spectra for cleaned copper, Cu_2O , and CuO have been published.⁶ The 2p peak appears as a doublet because of spin-orbit interaction. In CuO , each component of the doublet is broadened relative to metallic copper and Cu_2O because of multiplet splitting. Satellite peaks resulting from an electron shakeup process are observed on the high binding energy side of each doublet component in CuO . Inasmuch as both multiplet splitting and shakeup are associated with an unfilled d-band, these effects are seen only in CuO ($3d^9$) and not in metallic copper or Cu_2O in which the d-band is completely filled.^{7, 8} In fact, the Cu 2p photoelectron spectra of clean copper and Cu_2O are indistinguishable; however, the LMM Auger spectra of these materials are distinct. Use of both XPS and AES permits differentiation among all three materials.⁶

The clean copper spectrum in the published work discussed above was obtained from copper film deposited under high vacuum. Subsequent heating of the evaporated copper films in air, sometimes followed by partial reduction by heating in vacuum, produced adherent films of CuO and Cu_2O as desired. Our mechanically and chemically polished copper Cu 2p and LMM Auger spectra matched those published for clean copper. Copper oxidized with a heat gun and copper more heavily oxidized on a hot plate had spectra

matching those of Cu_2O and CuO , respectively. The observed shapes of the Cu Auger spectra agree well with published spectra. The energy shift of the most prominent Auger peak between "clean" Cu, Cu_2O , and CuO is somewhat less than the published values but is in the right direction. The spectra are not reproduced here.

Examination of the oxygen 1s photoelectron spectra revealed differences among the various copper specimens. Distinct components of the O 1s spectra were resolved by fitting Gaussian peaks to the experimental curves. Each observed spectrum could generally be reproduced by superposition of two Gaussian peaks, although, in some instances, an oxygen spectrum contained one or three components. Average peak positions and widths [defined as the full width at half maximum (FWHM)] are given in Table I. There is some evidence of a peak at about 532.5 eV with FWHM of 2.5 eV on both mechanically and chemically polished specimens, but this peak did not have sufficient intensity for satisfactory resolution.

Photomicrographs of clean and oxidized copper surfaces to which MoS_2 had been applied are shown in Fig. 2. Cellophane tape was applied, and removed, three times to these burnished specimens in order to remove loose MoS_2 particles, which can deceive the observer when making assessments of coverage. A qualitative assessment of the degree of surface coverage of burnished MoS_2 indicated that coverage was less on both oxidized surfaces (Cu_2O and CuO) than on copper surfaces that had not been deliberately oxidized.

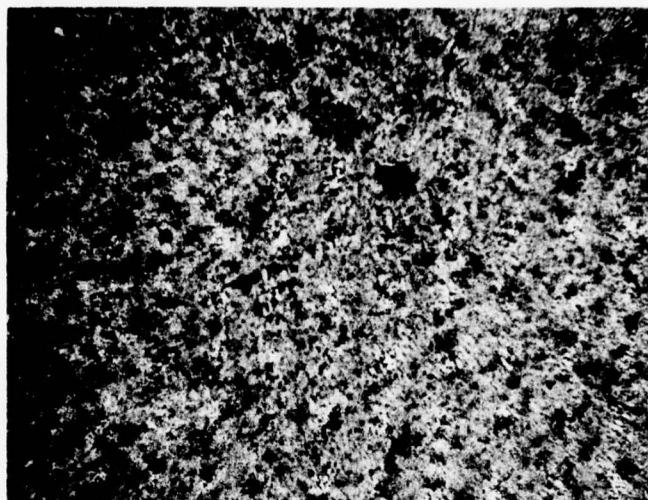
B. TITANIUM

The 2p photoelectron spectrum of titanium consists of a spin doublet with components corresponding to the $2p_{1/2}$ and $2p_{3/2}$ energy levels. All

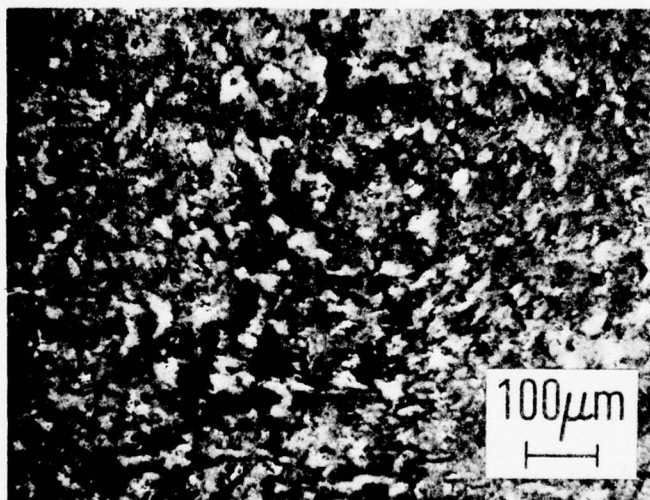
Table I. Oxygen Spectra on Copper

Specimen preparation	Component 1		Component 2	
	Position, eV	FWHM, ^a eV	Position, eV	FWHM, ^a eV
Mechanically polished	531.4 ± 0.2	2.2 ± 0.2	530.0 ± 0.1	1.2 ± 0.1
Chemically polished	532.0 ± 0.2	2.6 ± 0.1	530.6 ± 0.2	1.7 ± 0.5
Lightly oxidized	531.4 ± 0.4	2.2 ± 0.3	530.0 ± 0.3	1.2 ± 0.2
More heavily oxidized	531.1 ± 0.1	2.2 ± 0.1	529.5 ± 0.3	1.2 ± 0.1

^aFull width at half maximum



a



b

Fig. 2. Photomicrographs Illustrating Differences in Adhesion of MoS₂ on (a) Chemically Polished "Clean" Copper and (b) Oxidized Copper (Heated on a Hot Plate in Air)

specimens examined in this study, viz, mechanically and chemically polished titanium, oxidized titanium metal, and TiO_2 single crystals, have this characteristic 2p spin doublet with a peak shift that indicates the titanium is oxidized.⁹ On the mechanically polished specimens, 2p peaks from the underlying zero-valent metal were visible, which indicated that the oxide film was thinner in this case than for the chemically cleaned (in H_2SO_4) titanium. Electron-excited LMM Auger spectra also confirmed, by comparison with the literature, that titanium was present as TiO_2 at all specimen surfaces.¹⁰

The O 1s photoelectron spectrum on Ti/ TiO_2 specimens consisted of two resolvable peaks, one centered at 529.8 eV (FWHM 1.4 eV) and the other at about 531.6 eV binding energy (FWHM 2.1 eV). The higher binding energy peak usually appeared as a shoulder on the 529.8 eV peak. Figure 3 shows an O 1s spectrum of oxygen on mechanically polished titanium that is typical of both chemically and mechanically polished titanium and of deliberately oxidized titanium metal. More significant results were obtained on TiO_2 single crystals. The O 1s spectra of oxidized and reduced (as described earlier) TiO_2 single crystals are shown in Figs. 4(a) and 4(b), respectively. Note that two peaks are apparent. On oxidized TiO_2 , the ratio of the area of the 529.8 eV peak to that of the 531.6 eV peak is about 1.7, whereas on the reduced surface, this ratio is about 2.9. These area ratios were determined by fitting two Gaussian curves to the data.

Burnishing experiments indicated quite conclusively that MoS_2 adheres more readily on the reduced than on the oxidized TiO_2 . This difference in

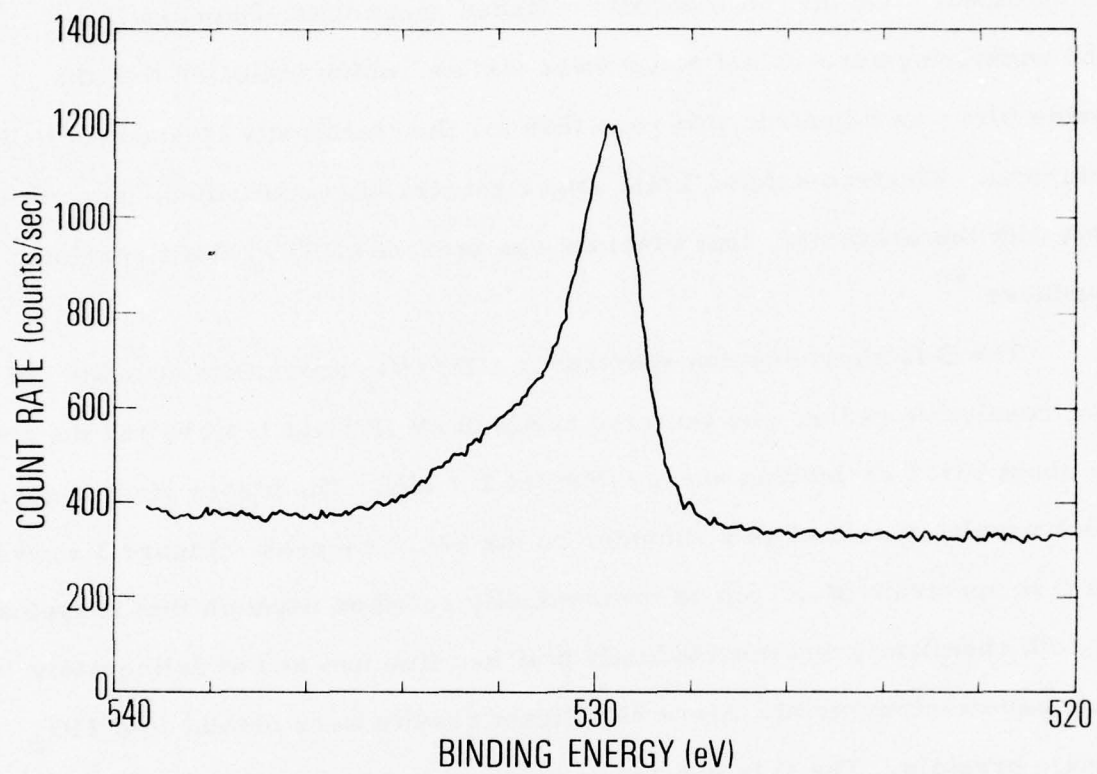


Fig. 3. O 1s Photoelectron Spectrum, Oxygen on Mechanically Polished Titanium Metal

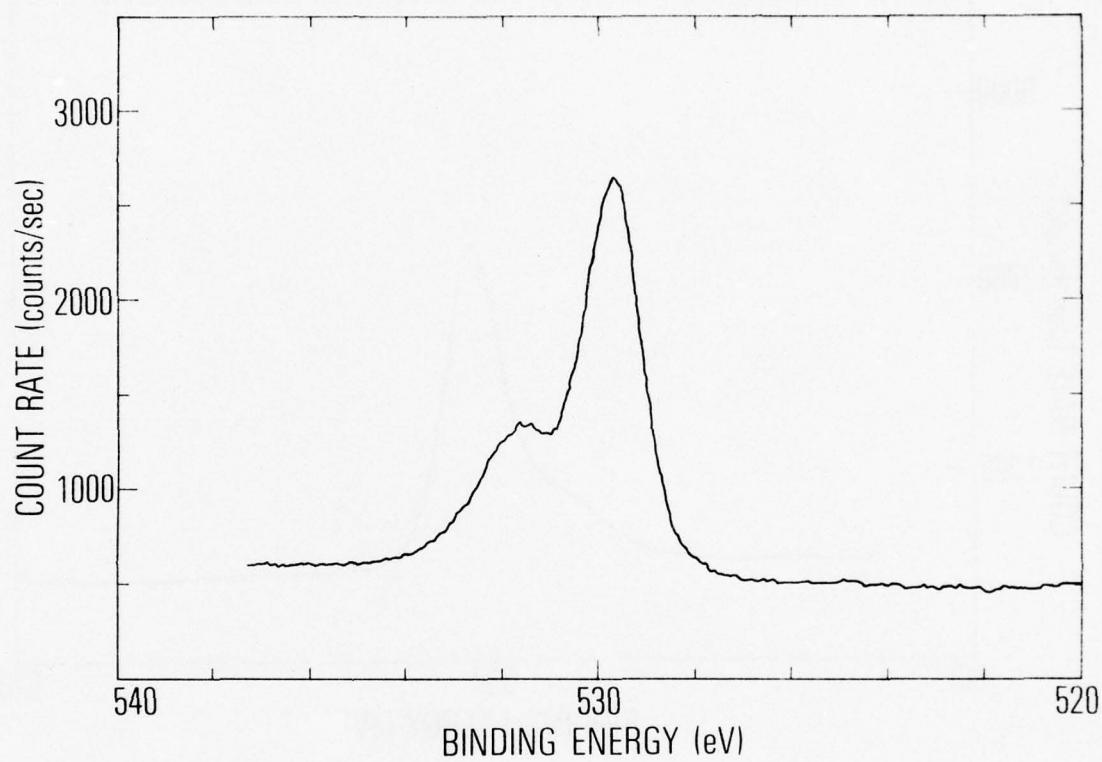


Fig. 4(a). O 1s Photoelectron Spectrum From TiO_2 Heated in Oxygen

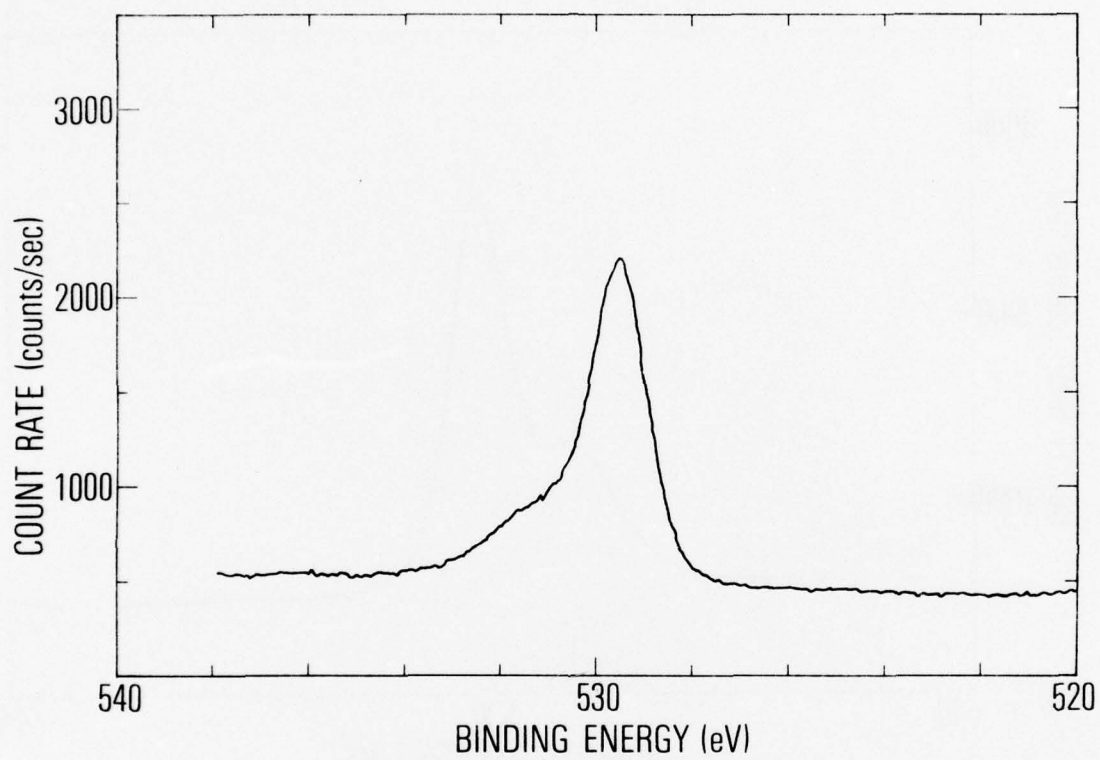
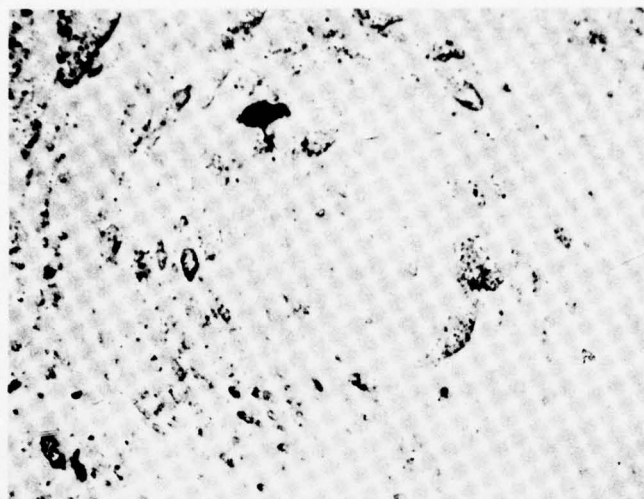


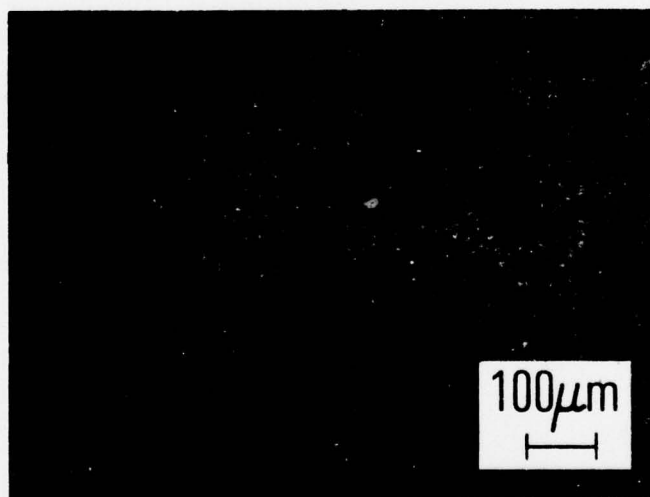
Fig. 4(b). O 1s Photoelectron Spectrum From TiO_2
Heated in Hydrogen

adhesion on the oxidized and reduced surfaces is shown in Figs. 5(a) and 5(b), respectively. There is essentially no adhesion of MoS_2 on the oxidized surface (although a few large pieces are evident), whereas the reduced surface in the burnished region has substantial MoS_2 coverage. It is difficult to see MoS_2 on the dark, nearly opaque reduced TiO_2 surface unless it is illuminated by reflected light at a low angle of incidence. Under these conditions, the MoS_2 is clearly visible.

Small pieces of ZrO_2 were available. MoS_2 was rubbed on the ZrO_2 with a "Q-tip" cotton applicator swab. Microscopic examination revealed absolutely no adhesion of MoS_2 on this oxide (the small sizes of the ZrO_2 pieces precluded both burnishing by our standard technique and XPS characterization).



a



b

Fig. 5. Photomicrographs Illustrating Differences in Adhesion of MoS_2 on (a) TiO_2 Heated in Oxygen and (b) TiO_2 Heated in Hydrogen

IV. DISCUSSION

The results presented in the preceding section and the general question of the adhesion of MoS_2 (and presumably other layer lattice compounds) to real metal surfaces, i.e., metals that may be covered by a surface oxide layer, may be understood through an extension of our previously published work. We discuss first the interpretation of our data on surface characterization, then consider the adhesion of MoS_2 to metal surfaces in light of this information, and finally comment on the prediction of MoS_2 adhesion.

A. SURFACE CHARACTERIZATION OF OXIDIZED METALS

1. COPPER

Distinct O 1s XPS peaks were observed on copper and oxidized copper. As electrons are transferred from oxygen to a cation, i.e., as the cation-oxygen bond strength increases, increasing negative charge facilitates the escape of photoelectrons from oxygen, and the position of the O 1s peak moves lower on the binding energy scale. For cations, the XPS binding energy increases as atomic charge increases. This point is mentioned here explicitly to preclude any possible misinterpretation during subsequent discussion.

It is reasonable to identify the most prominent, and lowest binding energy, peak in the O 1s XPS spectrum of known (from Cu XPS and Auger measurements) oxide surfaces as arising from lattice oxygen, O^{2-} . From Table I, this peak occurs at 530.0 ± 0.3 and 529.5 ± 0.3 eV in Cu_2O and CuO , respectively. The observed energy difference between O^{2-} in Cu_2O and CuO is in agreement with the literature, although the observed peak positions

differ somewhat when the literature values are corrected for a slightly different assumed hydrocarbon C 1s reference peak binding energy.¹¹ Calculation of the oxygen partial charges, following the method of Sanderson,¹² leads to the opposite conclusion; CuO should appear at a position higher than that of Cu₂O on the binding energy scale. However, the identity of the O²⁻ peak in CuO is reinforced by our observation of the O 1s spectrum of powdered CuO, which has its largest component at 529.2 eV with a FWHM of 1.3 eV.

Other peaks in the oxygen XPS spectrum of copper and oxidized copper have been identified with OH⁻ and strongly chemisorbed O⁻.¹¹ The 530.0 eV peak on mechanically polished copper, with its 1.2 eV width, could represent the initial stage of the formation of Cu₂O; however, Cu Auger measurements show only "metallic" copper. The ratio of the area of the 530.0 eV component to the area of the 531.4 eV component is about 0.5 on mechanically polished copper; lattice oxygen, if it occurred at all, would be a minority species. One specimen of chemically polished copper exposed to air and water for some minutes did visibly discolor, and oxygen peaks were found at 531.8 eV (FWHM 2.2 eV) and 530.1 eV (FWHM 1.2 eV). The peak at 531.4 eV may thus be due to OH⁻, in reasonable agreement with Robert, Bartel, and Offergeld.¹¹ In any event, the positive identification of these peaks is not essential to our argument concerning MoS₂ adhesion. The fact that oxygen peaks on both mechanically and chemically polished copper that have a higher energy on the XPS binding energy scale indicates that oxygen in the corresponding states is actually less tightly bound than is oxide oxygen. In the

case of surface OH groups, the fact that hydroxides generally lose water at temperatures much lower than the melting temperatures of oxides also supports the statement that the bonding of the OH groups to the surface is weak relative to the bonding of O^{2-} .

2. TITANIUM

The interpretation of our observations on titanium presents greater challenge. Both XPS and AES of clean and oxidized titanium metal identify the surface as TiO_2 , and yet MoS_2 adheres well to such specimens. The solution to this puzzle is provided by the XPS observations of TiO_2 single crystals. The most prominent peak in the O 1s spectrum of both TiO_2 heated in oxygen and TiO_2 heated in hydrogen at 529.8 eV binding energy is identified as the O^{2-} peak. The peak at 531.6 eV, which is much more prominent on the specimens heated in oxygen, is interpreted as representing more loosely bound surface oxygen rather than lattice oxygen, as in the case of copper. However, in contrast to copper, this oxygen is still bound tightly enough to prevent MoS_2 adhesion on oxidized surfaces.

Note that while oxygen associated with the 531.6 eV peak on TiO_2 is not removed by burnishing, oxygen with nearly the same XPS binding energy on copper is displaced. The observed XPS binding energy reflects changes in oxygen partial charge. Nearly equal XPS binding energies have been observed for oxygen adsorbed on a number of different metals, and this observation was taken to imply similar electronic environments.¹³ However, the oxygen-substrate bond energy, which determines ease of oxygen removal, is influenced by other factors in addition to partial charge, e.g., interatomic distance.

In a TiO_2 crystal (rutile), each oxygen atom is coordinated to three titanium atoms in the bulk. On a c-face, some oxygen atoms in the outer layer are coordinated to only one or two titanium atoms, whereas oxygen atoms in deeper layers are still coordinated to three titanium atoms. The O^{2-} oxide peak presumably arises from those oxygens coordinated to three titaniums. The 531.6 eV peak represents oxygen less tightly bound than bulk O^{2-} , probably oxygen bound to one (or two) titanium atoms. It is also possible that this less tightly bound oxygen may be in OH groups. When TiO_2 is heated in hydrogen, much of this less tightly bound oxygen is removed as H_2O , as evidenced by the decrease in magnitude of the 531.6 eV peak, which leaves behind mostly bulk O^{2-} and oxygen vacancies. On TiO_2 heated in O_2 , all possible oxygen sites are filled, not just those representing 3-coordinated O^{2-} ; thus, the peak at 531.6 eV grows in magnitude.

B. EXPLANATION OF MoS_2 ADHESION

As pointed out in our earlier work, the substrate metal-sulfur bond strengths, as determined, at least relatively, by substrate metal sulfide atomization energies, provide an estimate of the degree of adhesion of MoS_2 to be expected on different metal surfaces. However, in order for those metal-sulfur bonds to form, it is necessary that substrate metal atoms be accessible to the sulfur atoms of the molybdenum disulfide.

For metals such as copper, this accessibility probably arises from the relative ease with which surface oxygen may be displaced by MoS_2 . During the burnishing process, high local surface temperatures and pressures can be generated. Disruption of copper-oxygen bonds and formation of copper-sulfur bonds under such circumstances is more likely on surfaces where oxygen is in fact not as tightly bound as in the case of an oxide, e.g., on a clean copper surface, where the most common oxygen species may be OH.

For metals with a more tenacious surface oxide, e.g., titanium, surface oxygen vacancies provide reactive sites at which sulfur and the metal cations may form bonds. Metal ions are partially exposed at these sites.

C. PREDICTIONS OF MoS_2 ADHESION

Some general information on vacancy formation energies is available. This information contributes to a broader understanding of the adhesion mechanism of MoS_2 on oxide surfaces and, therefore, permits prediction of adhesive behavior.

For example, for oxygen defects to occur in an oxide, the cation should be stable in states with a valence that is lower than the valence found in the oxide. This requirement arises when an oxygen vacancy is produced according to the reaction



(L represents the lattice.) In order to preserve charge neutrality, the electrons combine with cations, at least in a formal sense, according to the expression



The oxides identified above as being oxygen defect materials do indeed have possible lower cation valence states, whereas oxides in which oxygen defects are not predominant, e.g., NiO, Cu₂O, do not. It should be noted that the higher oxidation states of the second and third transition series are, in general, more stable relative to their lower oxidation states than is the case for first-row transition elements.¹⁴ This implies that a second-row oxide such as ZrO₂ should have a lower oxygen vacancy concentration than its first-row analog TiO₂, and that MoS₂ should not adhere to ZrO₂ as well as it does to (defect) TiO₂. Our limited experimental data on ZrO₂ support this prediction.

It is reasonable to believe that the formation enthalpy of both anion and cation vacancies in an oxide lattice should be related to the enthalpy of formation of the bulk oxide since all three of these quantities depend ultimately on the strengths of the metal-oxygen bonds in the lattice. Such relationships have been observed and described empirically. For cation vacancies

$$\Delta H_{V_{\text{Me}}} = -\Delta H_f - 32 \text{ (Kcal/mole)} \quad (3)$$

and for oxygen vacancies

$$\Delta H_{V_{\text{O}}} = 2(E_a - 167) \text{ (Kcal/mole)} \quad (4)$$

where ΔH_f is the formation enthalpy of the bulk oxide and E_a is the atomization energy per mole of oxygen.¹⁵ The atomization energy is the energy required to transform one mole of oxide to isolated atoms. For an oxide Me_xO_y

$$E_a = \frac{1}{y} [-\Delta H_f + xL_s] + \frac{1}{2} D_{O_2} \quad (5)$$

where L_s is the vaporization energy of the metal and D_{O_2} is the dissociation energy of O_2 ($= 119.1$ Kcal/mole O_2). In our earlier work,⁴ atomization energies were calculated per equivalent weight of oxygen, whereas in Eq. (5), E_a is the atomization energy per mole, as required by Eq. (4). The factor of 2 difference is of no real consequence provided that definitions are applied consistently. The empirical expressions, Eqs. (3) and (4), have certain limitations. They are stated not to be valid for the B subgroups of the periodic table and are best applied to the A subgroups, the transition metals, and the 4f and 5f rare earths; they are true only for fully ionized vacancies, i.e., at high temperatures. Despite these limitations, the empirical expressions are useful to an understanding of departures from stoichiometry in oxides.

The formation energies of oxygen and cation vacancies and the ratio of oxygen to cation vacancy formation energies (denoted by α) are presented in Table II for some oxides in the first transition series. The ratio α does not provide an assessment of the total number of defects present; however, as α decreases, oxygen vacancies become the dominant defect. For a given element, the oxygen vacancy formation energy decreases, whereas the cation vacancy formation energy increases, i.e., α decreases, with increasing oxygen/metal ratio. In other words, in the higher oxides, oxygen vacancies are the dominant defect. This result is consistent with the previous statement

Table II. Cation and Anion Vacancy Formation Energies
in the First Transition Series

Oxide	$\Delta H_f^{\circ a}$ (Kcal/mole)	E_a (Kcal/mole O)	ΔH_{vO} (Kcal/mole vacancies)	ΔH_{vMe} (Kcal/mole vacancies)	$\alpha = \frac{\Delta H_{vO}}{\Delta H_{vMe}}$
TiO	-124.2	296	258	92	2.80
Ti ₂ O ₃	-363.5	256	177	166	1.07
TiO ₂ (rutile) ^b	-225.8	229	123	194	0.64
VO	-103.2	286	237	71	3.33
V ₂ O ₃	-293.5	239	145	131	1.11
V ₂ O ₄	-341.1	206	79	155	0.51
V ₂ O ₅ ^b	-370.6	183	32	169	0.19
Cr ₂ O ₃ ^b	-272.4	214	93	120	0.78
Cr O ₂	-143	178	23	111	0.21
Cr O ₃	-140.9	136		109	
MnO	- 92.07	219	104	60	1.72
Mn ₃ O ₄	-331.7	193	52	100	0.52
Mn ₂ O ₃	-229.2	181	27	197	0.14
Mn O ₂	-124.29	155		92	
Fe O	- 65	224	114	33	3.46
Fe ₃ O ₄	-267	201	68	78	0.87
Fe ₂ O ₃	-197	192	49	83	0.60
Co O ^b	- 56.87	218	102	25	4.10
Co ₃ O ₄	-213	189	44	60	0.73
Ni O ^b	- 57.3	220	105	25	4.16
Ni ₂ O ₃	-117.0	167	0	43	0

^aFrom National Bureau of Standards TN 270.

^bDenotes oxide usually found on the surface of the corresponding metal.

that oxygen defects are most likely for those oxides where the cation has stable lower valence states.

Departures from stoichiometry in oxides are well known.¹⁶ Experimentally, it has been verified that TiO_2 (often written TiO_{2-x}) is generally an oxygen deficient compound. Oxides of elements toward the end of the period, e.g., NiO , do not contain oxygen vacancies. They are metal-rich systems, i.e., interstitial atoms are present. The question of whether or not these extra metal atoms may have some role in facilitating MoS_2 adhesion has not yet been investigated. Expressions (3) and (4), and the values of α , calculated from these expressions, are perhaps meaningfully comparable only for elements within a single row of the periodic chart. If expressions (3) and (4) are evaluated for second-row elements, both ΔH_{vO} and ΔH_{vMe} are found to be larger than for analogous first-row oxides. Values of α are comparable.

V. SUMMARY AND CONCLUSIONS

It was demonstrated previously that the atomization energy of substrate metal-sulfur bonds provides an estimate of the degree of adhesion to be expected when MoS_2 is burnished onto different metal surfaces.⁴ In the present investigation, we have extended our earlier work and have explained the role of the surface oxide layer in the adhesion of MoS_2 . In order for substrate metal-sulfur bonds to form, it is necessary that sulfur have access to the metal. Our work indicates that, in the case of some oxides, e.g., copper, bond formation is accomplished through displacement of that oxygen less tightly bound than O^{2-} . For other metals, e.g., titanium, sulfur bonds to the substrate metal cations at oxygen vacancies.

The layered structure of MoS_2 , with its planes of sulfur atoms, undoubtedly facilitates the formation of substrate-sulfur bonds. In copper, sulfur atoms form a bridge between MoS_2 and the substrate. The MoS_2 -substrate interface on titanium might best be regarded as an incipient oxysulfide.

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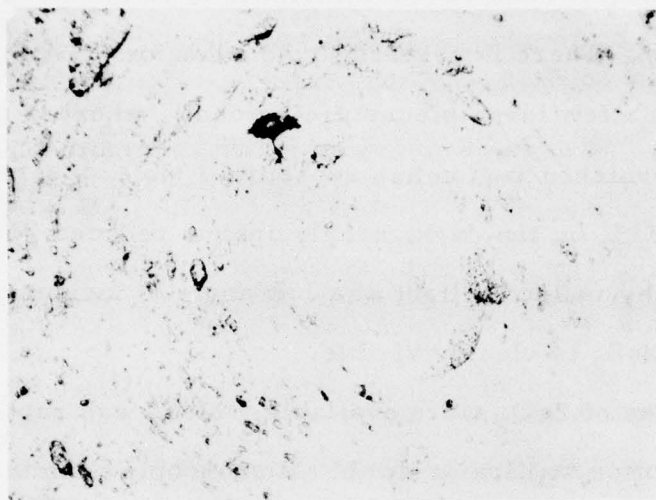
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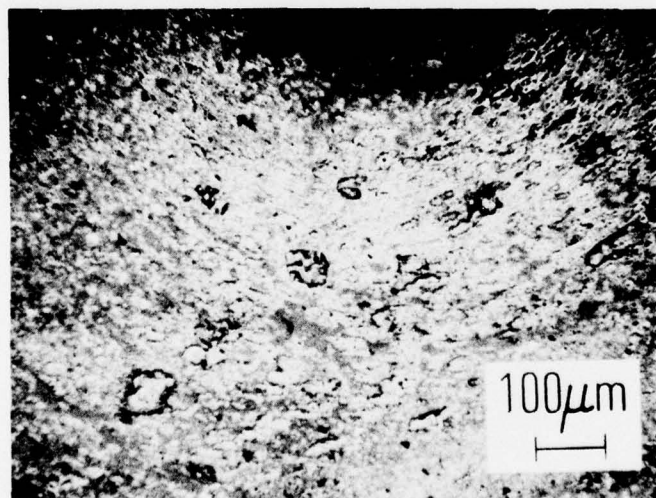
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adhesion on the oxidized and reduced surfaces is shown in Figs. 5(a) and 5(b), respectively. There is essentially no adhesion of MoS_2 on the oxidized surface (although a few large pieces are evident), whereas the reduced surface in the burnished region has substantial MoS_2 coverage. It is difficult to see MoS_2 on the dark, nearly opaque reduced TiO_2 surface unless it is illuminated by reflected light at a low angle of incidence. Under these conditions, the MoS_2 is clearly visible.

Small pieces of ZrO_2 were available. MoS_2 was rubbed on the ZrO_2 with a "Q-tip" cotton applicator swab. Microscopic examination revealed absolutely no adhesion of MoS_2 on this oxide (the small sizes of the ZrO_2 pieces precluded both burnishing by our standard technique and XPS characterization).



a



b

Fig. 5. Photomicrographs Illustrating Differences in Adhesion of MoS_2 on (a) TiO_2 Heated in Oxygen and (b) TiO_2 Heated in Hydrogen